Ordered mesoporous carbons (OMC) as supports of electrocatalysts for direct methanol fuel cells (DMFC): Effect of carbon precursors of OMC on DMFC performances

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Received 9 November 2005; received in revised form 15 February 2006; accepted 5 March 2006
Available online 15 May 2006

Abstract
This paper presents the effect of graphitic character of ordered mesoporous carbons (OMCs) on the performances of OMC supported catalysts for direct methanol fuel cells (DMFC). Two OMC samples with hexagonal mesostructure were prepared from phenanthrene and sucrose by nano-replication method using mesoporous silica as a template. Structural characterizations revealed that both OMCs exhibited large BET surface area and uniform mesopores, while the OMC synthesized from phenanthrene exhibited lower sheet resistance than the OMC derived from sucrose. The Pt nanoparticles were supported on both OMCs with very high dispersion, as the particle size was estimated under 3 nm despite high metal loading of 60 wt.%. In DMFC single cell test, the OMC supported Pt catalysts exhibited much higher performance than the commercial catalyst, which may be attributed to the high surface area and uniform mesopore networks of OMC. In particular, it was found that the performance of OMC supported catalysts can be significantly enhanced by lowering the resistance of OMC.

Keywords: Ordered mesoporous carbon; Sheet resistance; Platinum; Direct methanol fuel cell; Cathode catalyst

1. Introduction
Owing to its characteristics such as a high energy density, green emissions, convenient refueling of liquid fuel, and ambient operation conditions, direct methanol fuel cell (DMFC) is considered as a promising power source for the next-generation portable electronics that demand high power and long operation time [1–3]. However, there are many obstacles to be overcome for the commercialization of the DMFC system as real portable power source. In particular, low performance of DMFC system is a major problem, which in turn triggered a great deal of efforts to enhance the performance of DMFC system. The majority of the previous works have been focused on the development of electrode materials, including new electrocatalysts for anode and cathode [4–6], new proton conducting polymers [7], and on the improvement of the efficiency of the membrane electrode assemblies (MEA) [8]. With regard to the development of electrocatalysts, several strategies have been pursued to increase the catalytic activity of fuel cell electrode reactions; one of the attempts is the exploration of new catalyst composition which mainly deals with development of binary and ternary alloys of platinum to improve the kinetics of electrode reactions [9,10]. The preparation of highly dispersed metal nanoparticles is also being carried out to enhance catalytic activity by increasing the number of catalytically active sites [6]. Finally, new types of carbon materials are used as supports for DMFC catalyst to exploit the advantageous structural properties of such carbon materials [11–24].

Electrocatalysts for fuel cell electrodes are mostly composed of Pt-based metal nanoparticles, which are usually dispersed on porous carbon supports. For the fuel cell applications, carbon supports should have several characteristics, which include high surface area for finely dispersing catalytic metal particles, high electrical conductivity for providing electrical pathways, mesoporosity for facile diffusion of reactants and by-products, and water handling capability for removing water generated at
the cathode. Recently, nanostructured carbons, including carbon nanotubule [11], carbon nanofiber [12,13], carbon nanotube [14,15], macroporous carbon [16,17], graphitic carbon nano coil [18,19], and ordered mesoporous carbon (OMC) [20–24], have been utilized as catalyst supports for fuel cells. The electrocatalysts employing such nanocarbon supports exhibited promising catalytic activities toward methanol oxidation and oxygen reduction reactions, which were attributed to the unique structural characteristics inherent in the nanocarbons, including high conductive framework structure by graphitization, periodic pore structure in mesoporous or macroporous regime, and high specific surface area.

Among a variety of nanostructured carbons, in particular, the OMCs are highly intriguing as carbon supports for fuel cell applications from the viewpoint of pore structure. OMCs are prepared by the nano-replication method [25,26] using ordered mesoporous silicas (OMS) as templates [27,28]. The structure of OMC is constructed with periodic arrays of carbon nanorods or nanopipes with uniform mesopes existing between them. OMCs exhibit high specific surface areas up to 2000 m² g⁻¹, uniform pore diameters in the range of 2–10 nm, and high thermal, chemical and mechanical stabilities. Therefore, they have received great technological attention for the development of fuel cell catalysts [20–24], adsorption systems [29], double-layer capacitors [30,31], and new nanotemplates [32,33].

For the fuel cell applications, Ryoo et al. [20] first recognized the possibility of using OMC as a carbon support, and reported that Pt nanoparticles supported on CMK-5 mesoporous carbon exhibited superior electrocatalytic mass activity toward oxygen reduction in half-cell configuration compared to the catalyst dispersed on conventional carbon black support. Chan et al. [21] and Zhao et al. [22] reported that the metal nanoparticles supported on CMK-3 mesoporous carbons showed promising electrocatalytic activities for oxygen reduction and methanol oxidation reactions. The DMFC single cell performance was demonstrated using the Pt supported on CMK-3 carbon as cathode catalyst [23]. Recently, we reported that Pt particles supported on CMK-3-type OMC exhibited higher performance in DMFC single cell test compared to the Pt black catalyst [24]. Although aforementioned works demonstrated the possibility of OMCs as a new type of carbon supports for DMFC, there remains many opportunities to improve the performance of DMFC. In particular, considering the importance of graphitic character (i.e., electrical conductivity) of carbon supports for DMFC applications [18,19], if the carbon frameworks of OMCs can be more graphitized, the performance for fuel cell should improve. In this regard, the efforts to synthesize OMCs with graphitic framework, which rely on the introduction of new preparation method like CVD [23,34], or the uses of aromatic compounds includingacenaphthene [35], naphthalene, anthracene and pyrene [36], and polymeric compounds like mesophase pitch [37] as carbon precursors, have recently begun to appear.

The present work was undertaken to investigate how the graphitic character of carbon frameworks of OMC affect on the DMFC performance. For this purpose, new OMC was synthesized using aromatic compound, phenanthrene, as a carbon precursor. The physicochemical properties of phenanthrene-derived OMC (POMC) were compared with those of OMC synthesized from sucrose (SOMC). The performances of Pt-loaded OMCs in comparison with the commercial catalyst were evaluated using electrocatalytic activity measurements for oxygen reduction reactions and DMFC single cell tests, and the correlation between the structural characteristics of OMCs and electrocatalytic activities were suggested.

2. Experimental

2.1. Synthesis of OMS and OMC

In the present work, hexagonally ordered, large pore OMS was used as a template for the synthesis of OMCs. The synthesis of OMS was performed following the reported method for MSU-H mesoporous silica with slight modification [38], which used Pluronic P123 triblock copolymer (Aldrich) as a supramolecular template and sodium silicate as a silica source under near neutral condition. The silica source, sodium silicate solution of Na/Si = 2.5 (10 wt.% SiO₂), was prepared from colloidal silica Ludox HS-40 (Aldrich, 40 wt.% SiO₂), NaOH, and distilled water. In a typical synthesis of OMS, P123 triblock copolymer and sodium silicate solution were mixed in deionized water, and the mixture was stirred at ambient temperature in a water-jacketed flask. To this mixture, acetic acid (JT Baker) diluted with deionized water was added to polymerize the silicate species. The resulting gel mixture had a molar composition of 1 SiO₂:0.017 P123:2.595 acetic acid:255 H₂O. The gel mixture was stirred at 318 K for 20 h and placed in an oven at 373 K for 24 h under static condition. The silica precipitate was filtered, washed with distilled water, and dried in a freeze-dryer. The product was finally calcined in static air at 823 K for 3 h. The hexagonally ordered OMCs were replicated from the above-synthesized OMS template, using two kinds of carbon precursors, phenanthrene and sucrose. The synthesis of OMC derived from phenanthrene (POMC), reported here for the first time, was performed in a similar way with the synthesis of CMK-3 mesoporous carbon [36,39]. The carbon precursor solution was prepared by dissolving a 0.7 g of phenanthrene and 2.1 g of p-toluene sulfonic acid in 7 ml of acetone. The precursor solution was divided into three portions. After impregnating the precursor solution into 1 g of OMS template by incipient wetness, the mixture was dried at 373 K and subsequently at 433 K. The impregnation-drying step was repeated twice more to completely infiltrate the internal pores of OMS template with carbon sources. The mixture was then carbonized while heating to 1373 K under nitrogen flow for 2 h. Finally, the silica templates were dissolved at room temperature using 10% HF in H₂O–ethanol solution. The OMC from sucrose (SOMC) was synthesized following the reported method for CMK-3 carbon [24,39]. The carbonization and HF treatment were performed in the same way with the POMC synthesis.

2.2. Preparation of OMC supported Pt catalyst [40]

Half gram of OMC sample (POMC or SOMC) was mixed with 1.5 ml acetone containing H₂PtCl₆·x H₂O (Umicore) by
incipient wetness method. The amount of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ in the solution was controlled to obtain a metal loading of 60 wt.%. After being dried in a 333 K oven overnight, the impregnated OMC material was heated in a $\text{H}_2$ flow to 473 K and kept for 2 h at same temperature. The adsorbed hydrogen was removed by heating to 623 K and kept for 2 h under nitrogen flow. The samples thus prepared were denoted as Pt/POMC and Pt/SOMC.

2.3. Characterization methods

The X-ray diffraction (XRD) patterns were obtained by Philips X’pert Pro X-ray diffractometer equipped with a Cu Kα source at 40 kV and 30 mA. Transmission electron microscope (TEM) images were taken with the G2 FE-TEM Tecnai microscope at an accelerating voltage of 200 kV. Scanning electron microscope (SEM) images were obtained by using Hitachi S-4500 field emission scanning electron microscope operating at 20 kV. Nitrogen adsorption experiments were performed at 77 K using a Micromeritics ASAP 2010 system. Surface areas of the samples were calculated using the BET equation, while pore size distributions were estimated by BJH (Barrett–Joyner–Halenda) method from adsorption branches of isotherms. Electrical sheet resistances were measured by four-point probe method using a Changmin Tech. CMT series at room temperature. Sample powders were compressed at 75.4 kgf cm$^{-2}$ for measurements.

2.4. Electrochemical characterization

Electrochemical measurements were conducted on a Solartron 1287A Potentiostat, with three-electrode cell using a Pt mesh and an Ag/AgCl (in saturated KCl) as counter and reference electrode, respectively. The working electrode was prepared by painting the catalyst ink, composed of the catalyst and Nafion® ionomer in water and iso-propanol, onto carbon paper, and drying the ink-coated carbon paper at 353 K for 1 h in vacuum oven. To estimate the electrochemically active surface areas of catalyst samples, cyclic voltammetries (CV) were performed in 0.1 M $\text{HClO}_4$ solution, which was purged with $\text{N}_2$ gas before measurements. The potential sweep range was from $-0.1$ to 1.4 V versus normal hydrogen electrode (NHE) and the scan rate was 5 mV s$^{-1}$. The activities of supported catalysts toward oxygen reduction reaction (ORR) were measured in $\text{O}_2$-saturated 0.1 M $\text{HClO}_4$ solution, with the potential range of 0.5–1.1 V versus NHE and the scan rate of 1 mV s$^{-1}$.

2.5. DMFC single cell test

The catalyst ink for cathode was prepared by dispersing the Pt/OMC electrocatalysts with Nafion® ionomer in alcohol solution. The catalyst ink was sprayed onto the gas diffusion layer to form a catalyst layer with 2 mg cm$^{-2}$ Pt loading. For comparative study, the cathode catalyst layer was also prepared with commercial Pt/C catalyst (HiSpec 9100, Johnson Matthey). The anode catalyst layer was prepared in the same way with the cathode layer, using PtRu black (HiSpec 6000, Johnson Matthey) with 6 mg cm$^{-2}$ loading. The MEA was fabricated by hot pressing the cathode and anode on the either side of a Nafion® 115 membrane. Single cell tests were conducted at 323 K using the MEA with 10 cm$^2$ of reaction area, and 1 M $\text{MeOH}$ for anode and dry air as fuels for anode and cathode, respectively. Potential versus current density plots were obtained by potentiodynamic measurement from open circuit voltage to 0.2 V.

3. Results and discussion

3.1. Synthesis and characterizations of OMS and OMC

In the present work, OMS was prepared following the synthesis method for MSU-H silica reported by Pinnavaia et al. [38], using cost-effective sodium silicate as a silica source. Two OMCs were replicated from the OMS nanotemplate, using phenanthrene and sucrose as carbon sources. Fig. 1 displays powder XRD patterns of OMS template and OMC replicas. The calcined OMS exhibited three, well-resolved XRD peaks, which can be assigned to (1 0 0), (1 1 0), and (2 0 0) diffractions of 2D hexagonal $p6mm$ symmetry. The unit cell dimension of OMS calculated from (1 0 0) diffraction was 12.0 nm. OMC samples, POMC and SOMC, replicated from OMS template, also showed XRD patterns of 2D hexagonal $p6mm$ mesostructure, with unit cell sizes 11.0 and 10.7 nm for POMC and SOMC, respectively. The XRD peaks in OMCs slightly shifted to higher diffraction angle (i.e. decreased unit cell dimension), compared to those of OMS, which was previously attributed to the structural shrinkage of carbon frameworks during the high-temperature carbonization [39]. In addition, it should be noted that the unit cell parameter for POMC is higher than SOMC, indicating that the POMC underwent less frameworks shrinkage than SOMC.
The change of morphology and pore structure during carbon replication was examined using SEM and TEM images, as displayed in Fig. 2. The SEM image of OMS in Fig. 2a shows that OMS is composed of spherical 200–300 nm particles. POMC (Fig. 2b) also exhibits similar particle morphology and size with OMS, indicating that the particle shape was maintained during the carbonization and subsequent removal of OMS template without any significant modification or alteration. The internal pore structures of OMS and POMC were observed by TEM images, as shown in Fig. 2c and d. TEM image for OMS (Fig. 2c) displays that uniform mesopores are periodically arranged along and perpendicular to the direction of the hexagonal pore arrangement. TEM image of POMC in Fig. 2d clearly reveals that the pore structure of the carbon is exactly an inverse replica of OMS, in that the pores and the walls of OMS were converted to carbon nanorods and mesopores of POMC, respectively. SEM and TEM images of SOMC (not shown) also exhibited similar particle morphology and pore structure with those of POMC.

The pore structures of OMS and OMCs were further investigated using N₂ adsorption experiments. Fig. 3 illustrates the N₂ adsorption–desorption isotherms, and corresponding pore size distribution curves calculated from adsorption branch of isotherms by BJH method for OMS and OMC samples. The isotherms of POMC and SOMC were shifted upward by 300 and 500 cm³ g⁻¹, respectively. The values of the BET surface areas, total pore volumes, and pore sizes are listed in Table 1. The OMS template exhibited typical Type IV isotherm with H1 hysteresis, as reported earlier [38]. The steep increase of N₂ uptake in adsorption branch in the partial pressure of 0.80–0.90 indicates that the mesopore of OMS template is quite uniform and well defined. The BET surface area of OMS template is 451 m² g⁻¹ and pore volume is 1.27 cm³ g⁻¹, while the pore diameter calculated from the adsorption branch of isotherms

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (nm)</th>
<th>δBET (m² g⁻¹)</th>
<th>V_t (cm³ g⁻¹)</th>
<th>w_{BJH} (nm)</th>
<th>R (mΩ cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMS</td>
<td>12.0</td>
<td>451</td>
<td>1.27</td>
<td>12.2</td>
<td></td>
</tr>
<tr>
<td>POMC</td>
<td>11.0</td>
<td>884</td>
<td>0.86</td>
<td>4.0</td>
<td>54</td>
</tr>
<tr>
<td>SOMC</td>
<td>10.7</td>
<td>1147</td>
<td>1.20</td>
<td>4.0</td>
<td>202</td>
</tr>
</tbody>
</table>

*: Notation: a, unit-cell parameter determined from XRD (1 0 0) interplanar spacing; δBET, BET specific surface area; V_t, total pore volume; w_{BJH}, pore diameter evaluated using the BJH method from an adsorption branch of isotherms; R, sheet resistance obtained by four-point probe method at the pressure of 75.4 kγ cm⁻².
is 12.2 nm. The \( \text{N}_2 \) isotherms of two OMC replicas, POMC and SOMC, exhibited similar shapes, where capillary condensation occurred in the partial pressure range of 0.4–0.6. Both OMCs exhibited the same pore size of 4.0 nm, while SOMC exhibited higher values of BET surface area and pore volume than POMC, as listed in Table 1.

The differences in the surface area and pore volume of two OMCs may be originated from the use of different carbon precursors. The POMC synthesized from aromatic precursor phenanthrene was expected to exhibit more graphitic character than SOMC, which in turn resulted in lower surface areas and pore volumes [35–37]. The graphitic character of OMCs was probed by sheet resistances. The sheet resistances were measured with four-point probe method by pressing the OMC samples at the pressure of 75.4 kgf cm\(^{-2}\). The obtained sheet resistances as in Fig. 4 and Table 1 reveal that the resistance of POMC is four-fold lower than that of SOMC. The results clearly indicate that the POMC is composed of more graphitized frameworks than SOMC. Sucrose is well-known hydrocarbon precursor, which leads to the formation of non-graphitic carbon structure after pyrolysis. Thus, aromatic phenanthrene molecule should afford OMC with more graphitic framework structure than sucrose [36].

### 3.2. Characterizations of Pt nanoparticles on OMCs

The unique structural characteristics of OMCs make them suitable as catalyst supports for DMFC applications [20–24]. For example, the high surface area of OMC, compared with the conventional carbon blacks such as Vulcan XC-72R and Ketjen Black, can provide sufficient surface functional groups or anchoring sites for the nucleation and growth of metal nanoparticles, thus metal catalysts can be prepared on OMC with high dispersion. Further, uniform mesopore structure of OMC would facilitate the diffusion of reactive molecules for electrochemical reactions. In the present work, two OMC samples exhibiting different graphitic character were used as supports for the preparation of Pt particles. Pt nanoparticles were supported on OMCs by impregnation of the Pt precursor (\( \text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O} \)) in acetone solution into the pores of OMCs via incipient wetness impregnation and subsequent reduction under \( \text{H}_2 \) flow. The total loading of Pt was controlled as high as 60 wt.%, because electrode catalyst for DMFC application requires generally very high metal loading [40].

Fig. 5 shows the XRD patterns for 60 wt.% Pt loaded POMC and SOMC catalysts. Both XRD patterns for both catalysts exhibit distinct peaks at around \( 2\theta = 39.8^\circ, 46.3^\circ, 67.5^\circ, \) and \( 81.3^\circ \), which correspond to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) plane of face centered cubic (f.c.c.) structure, respectively. There is no evidence of peak related to the oxide of Pt, indicating that the Pt precursor was completely reduced by \( \text{H}_2 \) treatment at 473 K. The average particle sizes of the catalysts estimated by Debye–Scherrer equation were 2.7 and 2.5 nm for Pt/POMC and
Pt/SOMC, respectively. Such sizes of Pt particles supported on OMCs are very small, considering that the metal content was as high as 60 wt.%.

The distribution and shape of Pt nanoparticles were observed with TEM. Fig. 6 exhibits the TEM images of 60 wt.% Pt/POMC and Pt/SOMC catalysts. The images show that the spherical Pt particles of 2–3 nm were uniformly dispersed along the carbon nanorods of OMCs without agglomeration of particles. Notably, TEM images clearly reveal that even after the metal loading, the internal, open mesopore structure of OMC was maintained. The mesopore structure in Pt/OMC catalysts was also accessed by N2 adsorption (not shown). The isotherms of Pt-loaded catalysts exhibited very similar shapes with those of OMC supports (Fig. 3a), except the decreased adsorption quantity [24]. Furthermore, pore size distributions of catalysts displayed the same peak maximum at 4 nm with those of OMCs. TEM images in combination with N2 adsorption experiments confirm that OMCs maintained mesopore structure after the introduction of Pt particles, which is important for facile diffusion of reactants during fuel cell electrode reactions.

3.3. Electrochemical activities and DMFC performances of Pt/OMC catalysts

The cyclic voltammograms (CVs) of Pt/OMC catalysts were obtained in N2-purged 0.1 M HClO4 solution (Fig. 7). The electrochemically active surface area of Pt/OMCs was obtained by integrating the total charge corresponding to the desorption peak of hydrogen, and normalizing with scan rate, Pt loading, and the charge value of 210 μC cm−2 for Pt surface [41]. Thus obtained active surface areas of Pt/OMC catalysts were 55.1 m2 g−1 for Pt/POMC and 66.2 m2 g−1 for Pt/SOMC, respectively, as listed in Table 2. The CV of commercial Pt catalyst supported on activated carbon with similar Pt loading (HiSpec 9100 catalyst; average Pt particle size maximum 2.8 nm [42]) was also obtained, and the active surface area was calculated as 42.3 m2 g−1.
Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt particle sizea (nm)</th>
<th>Pt surface areaa (m² g⁻¹)</th>
<th>Electrochemically active surface areab (m² g⁻¹)</th>
<th>Pt utilization efficiencyc (%)</th>
<th>Mass activity for ORRd A g⁻¹ Pt⁻¹</th>
<th>Current densitye (mA cm⁻²)</th>
<th>Power densityf (mW cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/POMC</td>
<td>2.7</td>
<td>103.8</td>
<td>55.1</td>
<td>53.1</td>
<td>1.01</td>
<td>119</td>
<td>48</td>
</tr>
<tr>
<td>Pt/SOMC</td>
<td>2.5</td>
<td>112.1</td>
<td>66.2</td>
<td>59.1</td>
<td>0.95</td>
<td>87</td>
<td>35</td>
</tr>
<tr>
<td>HiSpec 9100</td>
<td>2.8</td>
<td>100.1</td>
<td>42.3</td>
<td>42.3</td>
<td>0.74</td>
<td>53</td>
<td>21</td>
</tr>
</tbody>
</table>

a Estimated from XRD.

b Estimated from CV.

c Calculated by: area from CV × 100/area from XRD.

d Mass activity at 0.75 V vs. NHE.

e Current density and power density of DMFC single cells measured at 0.4 V and 323 K.

The theoretical specific surface area, \( S \) (m² g⁻¹) for Pt particles was also calculated from the crystalline size determined by the line broadening of XRD patterns, using the following equation [43]:

\[
S = \frac{6}{\rho (d)}
\]

where \( \rho \) is the density of platinum metal (21.4 × 10⁶ g m⁻³) and \( d \) is the diameter of the particle in nm determined from XRD. The Pt utilization efficiencies of the catalysts calculated from the theoretical surface areas obtained from the XRD and CV are also reported in Table 2. The surface area values calculated from the CV exhibit the loss of 40–60%, as compared to the surface area from the XRD. Such loss of surface area from the Nafion® impregnated Pt/C catalysts may be attributed to the blocking or anchoring of the Nafion® on the surface of Pt particles and to the inaccessibility of the proton to the Pt surfaces present in the interface of the Pt crystallites and the carbon support [44]. It should be noted that the Pt utilization for Pt/OMC catalysts is higher than that of HiSpec 9100 catalyst by 10–17%. The difference in the efficiency of Pt utilization between the supported catalysts is presumably originated from the porous structure of carbon supports. In the mesoporous carbon supported Pt catalysts, Pt particles are mostly attached on the surface of open mesopore walls with some portions of particles buried in the micropores present in the carbon frameworks. In the case of HiSpec 9100 catalyst, where microporous activated carbon was used as carbon support, most of Pt crystallites exist within the micropores. The Pt particle present in the spaces of large mesopore are expected to expose more fraction of its surface, compared to the particles in the micropores.

The electrocatalytic activities of carbon supported catalysts toward oxygen reduction reaction were measured. Fig. 8 shows the cathodic branches of cyclic voltammograms measured in O₂-saturated 0.1 M HClO₄ solution at room temperature. The mass activities measured at 0.75 V versus NHE are 1.01, 0.95, and 0.74 A g⁻¹ Pt for Pt/POMC, Pt/SOMC, and HiSpec 9100, respectively. The results indicate that Pt/OMC catalysts exhibit higher ORR activity than HiSpec 9100 catalyst while two OMC supported Pt catalysts show similar catalytic activity. The electrochemically active surface areas and ORR activities of carbon supported Pt catalysts, which were obtained from CV in half-cell configuration, are mostly dominated by the intrinsic kinetics of catalyst particle itself. As the particle sizes of Pt supported on two OMCs were very similar, the surface areas and ORR activities of two Pt/OMC catalysts showed only a little difference.

To gain more practical implications of our catalysts, DMFC single cell tests were performed. The single cell performances of DMFC were evaluated at 323 K using Pt-supported carbons as cathode catalysts and PtRu black as anode catalysts. The polarization curves in Fig. 9 indicate that the Pt/POMC catalyst exhibit highest performance. The current densities at 0.4 V and 323 K were found to be 119, 87 and 53 mA cm⁻² for Pt/POMC, Pt/SOMC, and HiSpec 9100 catalyst, respectively. The corresponding power densities at 0.4 V and 323 K were 48, 35, and 21 mW cm⁻², respectively. Between the OMC supported Pt catalysts and commercial HiSpec 9100 catalyst, Pt/OMC catalysts produce much higher power density than HiSpec 9100 by about 65–130%. Considering that the particle sizes of Pt in three catalysts are very similar (see Table 2), the increased cell performance may be attributed to the unique structural properties of OMCs. Highly developed mesopore structure in OMC, compared with the primarily microporous nature of activated carbon, would enhance the diffusion and transport of reactants including
liquid fuel and oxygen gas. Thus, the formation of gas–liquid multi-phase boundary may be facilitated. Further, the H₂O generated in the cathode may be more favorably transported in the mesopore networks of OMCs than the micropores of activated carbon.

Another aspect to be examined is the comparison between the two OMC supported Pt catalysts. Despite two Pt/OMC catalysts exhibited very similar electrochemically active surface area and ORR activity, the cell performance of Pt/POMC surpassed Pt/SOMC by 50%. As described in previous sections, the pore structures of two OMC supports and sizes of Pt particles supported on OMCs were very similar. Therefore, it is suggested that the enhanced performance of Pt/POMC, compared with Pt/SOMC, may be originated from the lower sheet resistance (i.e. higher electrical conductivity) of POMC. Previously, Steigerwalt et al., investigated activities of PtRu nanoparticles supported on several types of carbon nanofibers and carbon nanotubes for DMFC single cell tests [13]. They claimed that activities of DMFC single cells parallel the trend of electrical conductivity of MEA. The results obtained in the present work further support their conclusion, in that the electrical conductivity of carbon support make a significant effect on the single cell performance.

4. Conclusion

The work described in this paper presented the effect of graphitic character of OMC supports, induced by the uses of different carbon sources, on the DMFC performance. Two OMC samples, POMC and SOMC, were prepared using phenanthrene and sucrose as carbon precursors. POMC and SOMC showed similar particle size, pore size, and high surface areas, whereas POMC exhibited four-fold decreased sheet resistance, compared with SOMC, indicative of the higher electrical conductivity. Two OMC supported Pt catalysts exhibited much higher performance in DMFC single cell test than commercial HiSpec 9100 catalyst. The enhanced cell performance of Pt/OMCs may be attributed to high surface area, uniform mesopore networks of OMC, which are believed to favor diffusion of reactants and consequently the formation of liquid–gas multi-phase boundary. Furthermore, we point out that the graphitic character of OMC is of significant importance in enhancing the DMFC cell performance, as Pt catalyst supported on more graphitic POMC exhibited better cell efficiency than Pt/SOMC.

The OMCs can provide a high flexibility of structural diversities, which include the modulation of graphitic character, mesopore size, OMC particle size, etc. In this work, the effect of graphitic character of OMC on the DMFC performance was investigated. We are currently investigating the correlation between the afore-mentioned structural parameters of OMC supports and DMFC performance, which would establish the rationale toward optimized structural parameters of OMC for DMFC applications.

Acknowledgements

J.M. Kim acknowledges for financial support from the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, KRF-2005-005-J11901).

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